

Supporting information for

Electrostatic Regulation of Zn²⁺ Ion Concentration on Electrodes and Its Impact on Electrochemical Performance

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1. Experimental section

Fabrication of APC

Al(OH)₃ was added to 60% H₃PO₄ in a 1:3 molar ratio under magnetic stirring at room temperature for 10 min. The resulting transparent liquid was APC.

Fabrication of ZAP-Zn anode

1 g of APC was added to 3 mL of absolute ethanol, which was stirred at room temperature for 5 min. The resulting mixture was then coated onto Zn foil using a 20 μm doctor blade. Subsequently, it was dried in a vacuum oven at 100 °C for 2 h to obtain the ZAP-Zn anode.

Synthesis of NVO

NVO was synthesized by a hydrothermal method. Initially, 0.321 g of NH_4VO_3 (Aladdin, $\geq 99\%$) and 0.58 g of $\text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ (Macklin, $\geq 99.5\%$) were weighed in a beaker. Then, 40 mL of deionized water was added, and the mixture was stirred magnetically at room temperature for 0.5 h to obtain a yellowish-green solution. The solution was then transferred into a high-pressure reactor and heated at 180 °C for 3 h. After cooling to room temperature, the obtained precipitate was centrifuged and cleaned several times with deionized water and anhydrous ethanol. Finally, NVO was obtained by drying in a vacuum drying oven at 60 °C for 24 h.

Synthesis of NVO cathode

NVO powder, carbon black, and polyvinylidene fluoride were mixed in a mass ratio of 7:2:1 in N-methyl pyrrolidone solvent. The mixture was then ground using a mortar and pestle for 15 min to obtain a homogeneous slurry. This slurry was uniformly coated onto a Ti foil using a doctor blade with a 120 μm gap and subsequently dried in a vacuum oven at 100 °C for 12 h to obtain the NVO cathode.

Electrochemical Tests

Galvanostatic charge/discharge tests for all coin cells were conducted using LANDCT2001A test system. Coin cells (2032 type) were assembled by fiberglass diaphragms and electrode pieces. Fiberglass diaphragms with electrolytes was placed in between the prepared cathode and Zn anodes in an open atmosphere. Each cell contained 130 μL electrolytes. The reversibility and cycle stability of NVO cathodes in the full cells were evaluated and tested in a voltage window from 0.4 to 1.8 V. In addition, CV and EIS were performed on a Metrohm (PGSTAT302N) Autolab electrochemical workstation. The CV of Zn||Ti cells were tested at a scanning rate of 2 mV s^{-1} from -0.2 to 1.5 V. The overpotential reported in this work is the arithmetic average value of the nucleation overpotential measured over the first 10 cycles in the time-voltage curve of the Zn//Zn cells.

MD simulations

MD simulations were conducted using Forcite module of BIOVIA Material Studio software. Components involved in simulation were processed using Forcite module

with a Functional of GGA/PBE to obtain reasonable structures. The force field parameters were using COMPASS III.

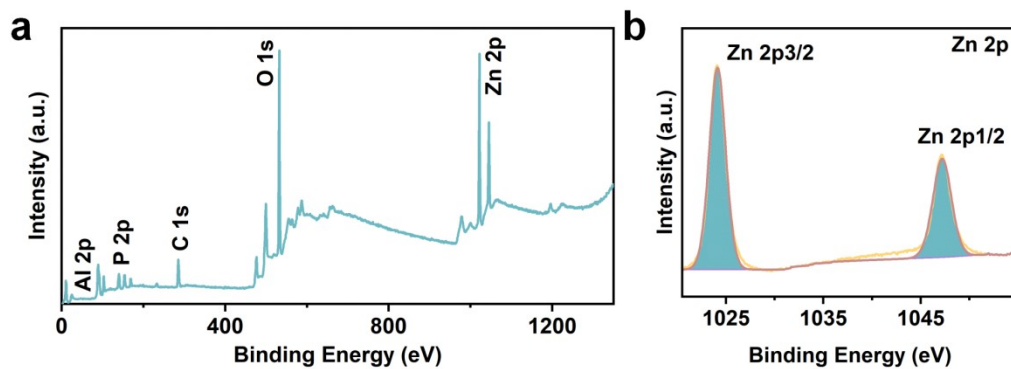


Figure S1. (a) The survey and (b) Zn 2p XPS spectra of ZAP-Zn.

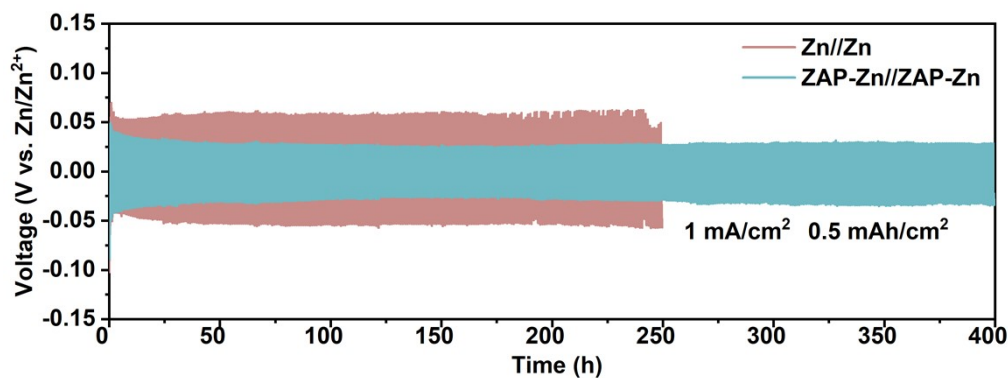


Figure S2. Long-term cycling performance of Zn//Zn and ZAP-Zn//ZAP-Zn cells at 1 mA cm⁻² and 0.5 mAh cm⁻² using 1 M ZnSO₄ electrolytes.

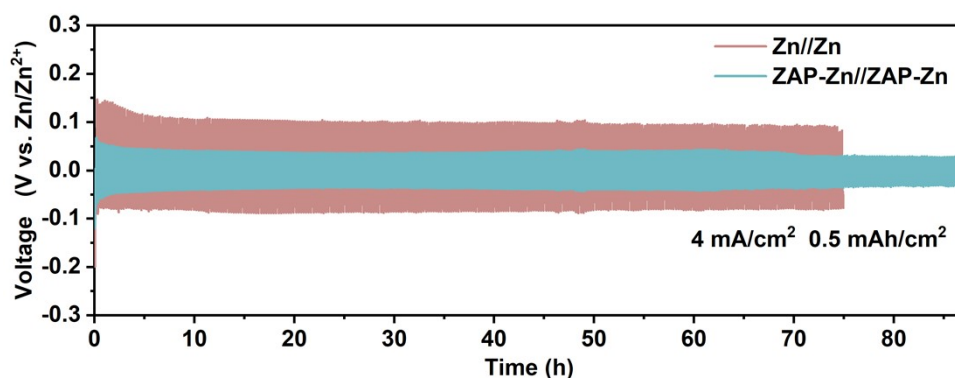


Figure S3. Long-term cycling performance of Zn//Zn and ZAP-Zn//ZAP-Zn cells at 4 mA cm⁻² and 0.5 mAh cm⁻² using 1 M ZnSO₄.

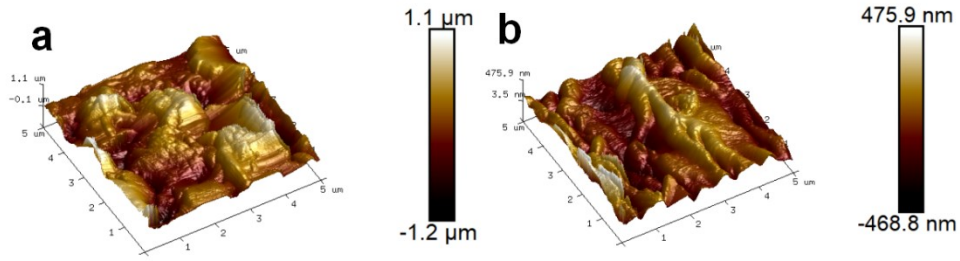


Figure S4. AFM of (a) Zn and (b) ZAP-Zn electrodes after 50 cycles.

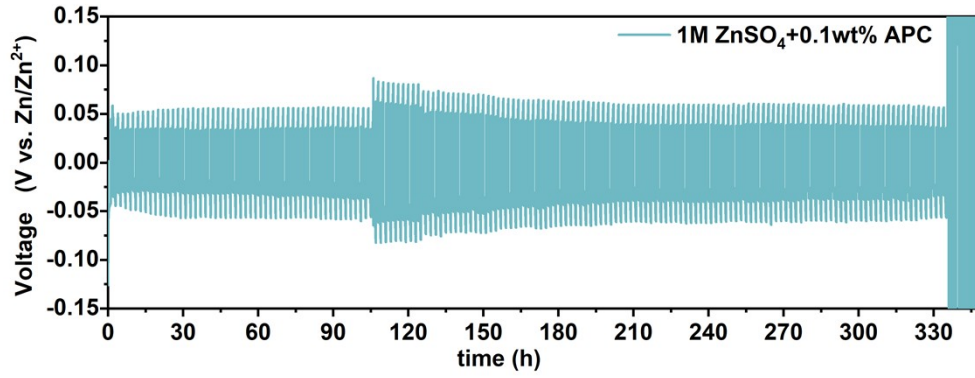


Figure S5. Long-term cycling performance of Zn//Zn symmetric cells with 1 M ZnSO_4 electrolytes containing 0.1 wt% APC.

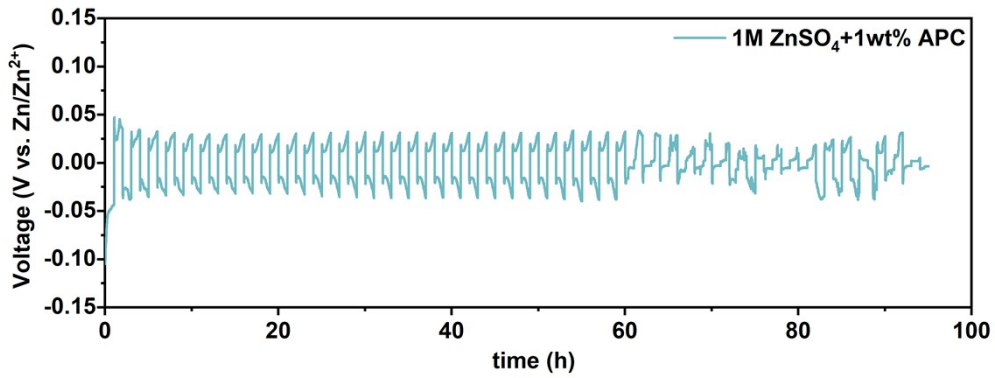


Figure S6. Long-term cycling performance of Zn//Zn symmetric cells with 1 M ZnSO_4 electrolytes containing 1 wt% APC.

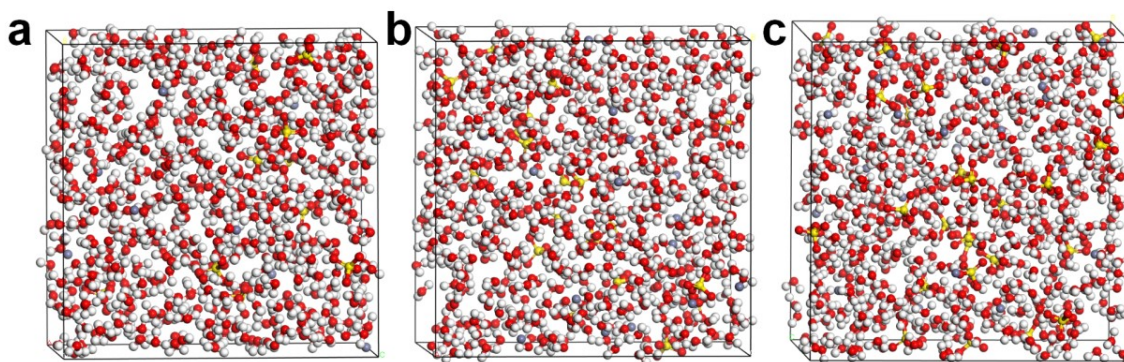


Figure S7. The solvation structures in (a) 1 M, (b) 2 M and (c) 3 M ZnSO_4 electrolytes.

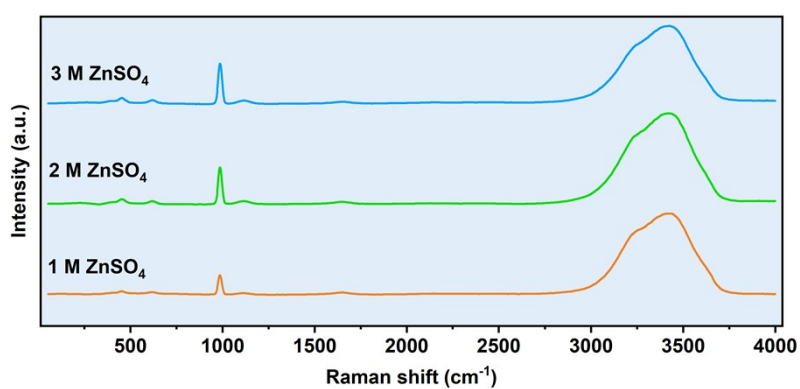


Figure S8. Raman spectra of ZnSO_4 electrolytes with varying concentrations.

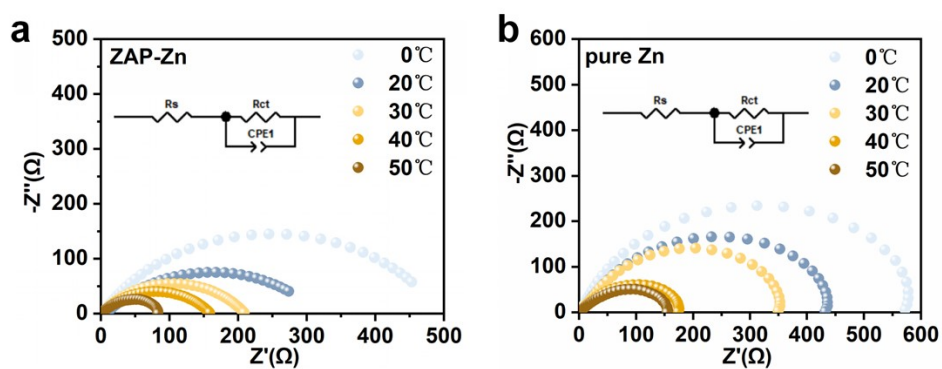


Figure S9. Temperature-dependent EIS of (a) ZAP-Zn//ZAP-Zn and (b) Zn//Zn cells with 1 M ZnSO_4 .

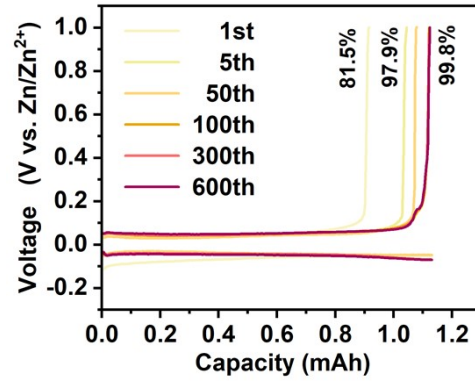


Figure S10. corresponding voltage profiles of Zn//Cu and ZAP-Zn//Cu cells in 1 M ZnSO₄.

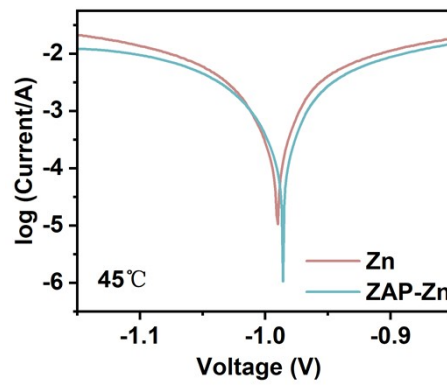


Figure S11. Tafel plots of Zn and ZAP-Zn electrodes in 1 M ZnSO₄ at 45 °C.

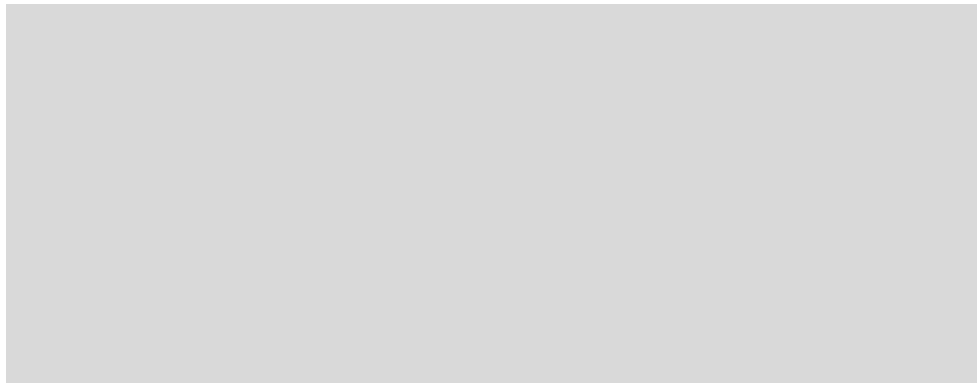


Figure S12. EIS measurements of (a) ZAP-Zn//ZAP-Zn and (b) Zn//Zn cells at various time intervals.

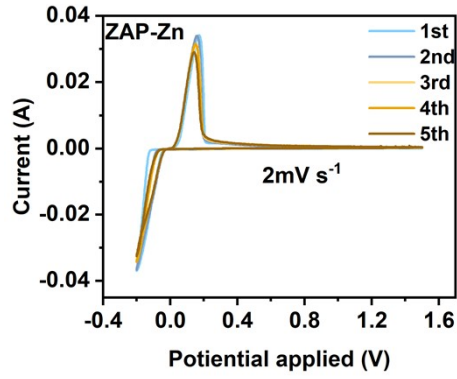


Figure S13. CV curves of ZAP-Zn//Ti cells.

Table S1. Cost of ZAP layer.

	cost
85% H ₃ PO ₄	0.067 \$/mL
Al(OH) ₃	0.014 \$/g
ZAP	8.1×10^{-4} \$ cm ⁻²

Table S2. The overpotentials of symmetric cells in ZnSO₄ electrolyte with varying concentrations.

	Overpotential of Zn//Zn (V vs. Zn/Zn ²⁺)	Overpotential of ZAP-Zn//ZAP-Zn (V vs. Zn/Zn ²⁺)
1 M ZnSO ₄	0.045	0.03
2 M ZnSO ₄	0.032	0.028
3 M ZnSO ₄	0.03	0.027

Table S3. Ionic conductivity of different electrolytes.

	σ
1 M ZnSO ₄	52.1
2 M ZnSO ₄	43.8
3 M ZnSO ₄	35.3

Ionic conductivity is calculated using the formula $\sigma = \frac{L}{R \cdot S}$, where σ is the ionic conductivity, R is the electrolyte resistance, L is the distance between the two

stainless steel electrodes, and S is the electrode area.

Table S4. Number of molecules used in MD simulations performed for different electrolytes.

	Zn ²⁺	SO ₄ ²⁻	H ₂ O
1 M ZnSO ₄	20	20	1112
2 M ZnSO ₄	40	40	1112
3 M ZnSO ₄	60	60	1112

Table S5. Corrosion voltage and corrosion current of Tafel plots of ZAP-Zn and Zn electrodes at different temperature in 1 M ZnSO₄.

		corrosion current (A)	corrosion voltage (V)
20 °C	ZAP-Zn	9.01e ⁻⁵	-0.951
45 °C	ZAP-Zn	1.58e ⁻⁴	-0.946
20 °C	Zn	1.12e ⁻⁴	-0.968
45 °C	Zn	2.09e ⁻⁴	-0.955